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Report No. 21

Bimonthly Progress Report for 1 July to 1 September 1962

THERMOELECTRIC MATERIALS

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SRI Project No. SU-2681

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Approved:

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I INTRODUCTION

This Progress Report describes the work performed under Contract NObs-77017 (Index Number NS-058-001) on thermoelectric materials for the period 1 July to 1 September 1962 and outlines the proposed effort for the next period.

II WORK PERFORMED

Cuprous Sulfide - Bismuth Sulfide--Measurements have been made to determine the Seebeck coefficient and resistivity of a 50 mol % Cu_2S and 50 mol % Bi_2S_3 composition. The pure compounds were melted together in an evacuated, sealed quartz tube for 24 hours at a temperature of 700°C , and then quenched to prevent segregation of components during solidification.

The solidified melt was ground to a powder in a mortar and loaded into the cell. Graphite electrodes were used to contact the melt and a helium atmosphere was maintained over the sample. During the run considerable decomposition occurred, as evidenced by sulfur depositing in the cooler regions of the apparatus. This composition is an n-type liquid although only slightly so at the higher temperatures. Table I presents the data--in chronological order since the sulfur content decreased with increasing time in the molten state. The Seebeck coefficients are referred to platinum; the temperature gradients impressed during Seebeck voltage determinations did not exceed 20°C .

It would appear that a loss of sulfur does not affect the Seebeck coefficient in this system appreciably but does lower the resistivity considerably. The implications of this are not clear, and further investigation is needed to develop more experimental data. This composition is not attractive from the power generation standpoint, but the n-type character of the liquid may indicate a direction which, if pursued, could result in an n-type material of interest.

Table I

CUPROUS SULFIDE - BISMOUTH SULFIDE
50 MOL-PERCENT

$T(^{\circ}\text{C})$	$S(\mu\text{V}/^{\circ}\text{C})$	$T(^{\circ}\text{C})$	$\rho(\Omega\text{-cm} \times 10^3)$
772	-24	756	7.51
777	-23	828	4.78
837	-7	891	2.77
897	+9	850	3.25
856	0	799	4.11
807	-12	773	4.70
794	-15	785	4.38
764	-25	756	5.07
744	-31	732	5.79
716	-41	705	6.79
689	-52	682	7.81
777	-21	768	4.59
831	-5	822	3.53
676	-50	753	4.57
659	-58	668	7.12
		650	7.94

Cuprous Sulfide - Nickel Sulfide--Measurements of the Seebeck coefficient and resistivity were made on the 50 mol % Cu_2S + 50 mol % NiS composition. Sample preparation was carried out in the same manner as described for $\text{Cu}_2\text{S} - \text{Bi}_2\text{S}_3$ composition except that a sulfur reservoir was attached to the tube and one atmosphere of sulfur pressure was maintained over the mixture held at 900°C for 16 hours. The solidified melt was ground in a mortar and the powder loaded into the cell. Graphite electrodes were used to contact the melt and a helium atmosphere maintained over the sample during the run. This composition is a p-type material of low resistivity and low Seebeck coefficient. Table II

Table II

CUPROUS SULFIDE - NICKEL SULFIDE
50 MOL-PERCENT

T(°C)	S(μ V/°C)	T(°C)	$\rho(\Omega\text{-cm} \times 10^{-4})$
920	+59	915	5.88
947	55	941	5.83
981	58	977	5.59
1006	60	1002	5.92
903	65	900	5.14
937	57	935	5.57
1003	60	934	5.56
1102	62	1000	5.59
1052	60	1099	5.92
962	55	1048	6.08
875	56	958	5.94
890	60	871	5.84
		885	5.31

presents the data obtained in chronological order; the Seebeck coefficient values are referred to platinum.

This composition has a low resistivity in comparison with cuprous sulfide. The Seebeck coefficient is too low for use as a power generation material, but an increase in the Seebeck coefficient might be obtained by maintaining a sulfur pressure over the sample.

Cuprous Telluride - Lead Telluride -- Measurements of the Seebeck coefficient and resistivity have been made on a 50 mol % Cu_2Te + 50 mol % PbTe composition. The n-type PbTe was furnished to us by Mr. Barmat of The General Instrument Corporation. The composition was prepared by heating the powdered Cu_2Te and PbTe in an evacuated, sealed quartz tube. The temperature was held at 800°C for 16 hours and the melt quenched to

prevent segregation during solidification. The sample was ground to a powder and loaded into the cell; graphite electrodes were used to contact the melt and an atmosphere of helium was maintained over the sample during the run. No significant decomposition occurred, as determined by the amount of tellurium deposited in the cooler regions of the cell up to the maximum temperature of 842°C. There was evidence that the quartz had been etched by the melt which indicates the presence of metallic lead or lead oxide. The melting point of this composition was determined visually, in a separate sealed quartz tube, to be 650-660°C. Table III presents the data obtained in chronological order, and the Seebeck coefficient values are referred to platinum. Impressed temperature gradients did not exceed 20°C in the Seebeck voltage determinations.

Table III

CUPROUS TELLURIDE - LEAD TELLURIDE
50 MOL-PERCENT

T(°C)	S(μv/°C)	T(°C)	ρ(Ω-cm x 10 ³)
683	+100	678	2.04
694	120	697	2.13
702	117	700	1.92
705	120	710	1.95
714	119	724	1.82
729	112	734	1.80
739	106	746	1.74
751	105	771	1.64
776	99	798	1.53
802	92	842	1.38
845	82	689	2.21
684	123	680	2.27
654	120	648	2.41
641	118	636	2.43
625	92	620	1.18
556	43	550	1.07


This composition is a p-type and not quite so promising as the $\text{Cu}_2\text{S} - \text{Cu}_2\text{Te}$ mixtures although it has a lower melting point.

III WORK PLANNED 1 SEPTEMBER TO 1 NOVEMBER 1962

Work will be continued on the Seebeck coefficient and resistivity under sulfur atmosphere for cuprous sulfide and mixtures with other sulfides.

IV CONTRIBUTORS

Mr. G. Withers and Dr. J. W. Johnson prepared various compositions and made electrical measurements.


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